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Effects of capping on the $Ga_{1-x}Mn_xAs$ magnetic depth profile

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Annealing can increase the Curie temperature and net magnetization in uncapped $Ga_{1-x}Mn_xAs$ films, effects that are suppressed when the films are capped with GaAs. Previous polarized neutron reflectometry (PNR) studies of uncapped $Ga_{1-x}Mn_xAs$ revealed a pronounced magnetization gradient that was reduced after annealing. We have extended this study to $Ga_{1-x}Mn_xAs$ capped with GaAs. We observe no increase in Curie temperature or net magnetization upon annealing. Furthermore, PNR measurements indicate that annealing produces minimal differences in the depth-dependent magnetization, as both as-grown and annealed films feature a significant magnetization gradient. These results suggest that the GaAs cap inhibits redistribution of interstitial Mn impurities during annealing. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1867292]

The emerging field of "spintronics" has motivated recent interest in developing high Curie temperature (T_C) ferromagnetic semiconductors. $Ga_{1-x}Mn_xAs$ is a possible candidate for spintronic applications, with a maximum achieved $T_C \approx 150$ K.[1,2] The ferromagnetic exchange in $Ga_{1-x}Mn_xAs$ results from coupling between Mn ions at Ga sites (Mn_{Ga}) that is mediated by holes self-generated by Mn_{Ga}.[3] However, Mn_{Ga} are partially compensated by other impurities, including Mn at interstitial sites (Mn_I).[4] Mn_I are double donors and are thought to exhibit an antiferromagnetic exchange interaction with neighboring Mn_{Ga} (Ref. 5)—making Mn_I highly disruptive to ferromagnetism.

Annealing of $Ga_{1-x}Mn_xAs$ can greatly increase T_C (Ref. 6) and the magnetization (M).[7,8] Understanding the mechanism of this annealing process is of utmost technological importance, in order to determine if T_C can be pushed further toward room temperature. A recent study has shown that capping $Ga_{1-x}Mn_xAs$ thin films with GaAs suppresses any enhancement of T_C or M associated with annealing.[9] This corroborated other recent work suggesting that annealing causes Mn_I to diffuse to the film surface, freeing additional Mn_{Ga} to participate in the ferromagnetic exchange.[2,10,11]

In Ref. 11, we used polarized neutron reflectometry (PNR) to show that optimal annealing of an uncapped 100 nm $Ga_{1-x}Mn_xAs$ film ($x=0.073$) not only increased T_C and M, but also changed the surface composition. Additionally, we found that the as-grown film had a pronounced gradient in M that increased from the substrate to the surface—a feature that was significantly reduced after annealing. We have since seen these effects reproduced in thinner (but otherwise similar), uncapped $Ga_{1-x}Mn_xAs$ films.[12]

We have now expanded our study to probe the effects of annealing on the *depth-dependent* properties of $Ga_{1-x}Mn_xAs$ capped with GaAs. Using molecular-beam epitaxy, a $Ga_{1-x}Mn_xAs$ sample was prepared by first depositing a 160 nm GaAs buffer layer on a [001] GaAs substrate at a temperature of 580 °C, then cooling the substrate to 230 °C and adding another 2.7 nm GaAs buffer layer, before depositing a 100 nm film of $Ga_{1-x}Mn_xAs$, and then a 9 nm GaAs cap. Using x-ray diffraction, the Mn_{Ga} concentration of the film was estimated to be $x=0.076$.[13] This sample was cleaved, and one piece was annealed in N_2 for 1 h at 270 °C (nominally the same conditions as in Ref. 11), while another piece was left as-grown. These pieces were further cleaved, providing separate specimens for PNR and superconducting quantum interference device (SQUID)-based magnetometry.

The net M of the samples, obtained using the magnetometer, is shown in Fig. 1. Fields were applied along a [110] direction. These measurements show that, in sharp contrast with uncapped samples, annealing does not improve the ferromagnetic properties (in agreement with Ref. 9). In fact, we observe that annealing is *detrimental* to the sample's ferro-

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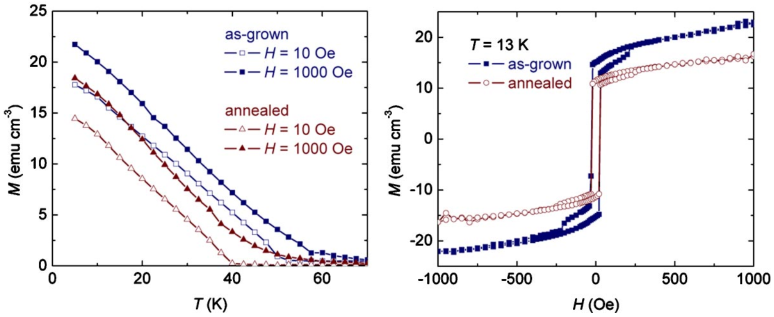

FIG. 1. (Color online) SQUID-based magnetometry results showing the net magnetizations of the capped as-grown and annealed films.

magnetic properties, as the low-field T_C is reduced from 53 to 40 K, and the high-field M at $T=13$ K drops from 23 to 17 emu cm^{-3}. Annealing of a similar uncapped $Ga_{1-x}Mn_xAs$ sample in the same oven at the same time as the capped sample resulted in a significant increase in T_C (from 40 to 90 K)—evidence that the GaAs cap is indeed responsible for ruining the beneficial effects of annealing.

PNR measurements were conducted using the NG-1 Reflectometer at the NIST Center for Neutron Research. A magnetic field of $H\approx 6.6$ kOe was applied in the plane of the sample along a [100] direction before cooling it to $T=18$ K. Neutrons were spin-polarized either parallel or antiparallel to H, and were specularly reflected from the sample. The non-spin-flip (R_{++} and R_{--}) and spin-flip (R_{+-} and R_{-+}) reflectivities were measured as functions of wave vector transfer Q. The data were corrected for Q-dependent sample illumination, and for instrumental background. The spin-flip scattering was minimal, and was used only to make polarization efficiency corrections to the data.

Figure 2 shows the corrected PNR data and fits in terms of spin asymmetry

$$SA=(R_{++}-R_{--})/(R_{++}+R_{--}), \tag{1}$$

which is a convenient quantity for gauging the sample magnetization parallel to H at different length scales. The spin asymmetries for capped the as-grown and annealed samples are very similar, as the oscillations for both are "smeared"—indicative of magnetic roughness.[11] The amplitude of the lowest-Q peak is larger for the as-grown sample, consistent with a slightly reduced net M after annealing.

Depth-dependent magnetic and structural properties can be deduced by fitting PNR data with a scattering length density (SLD) model.[14,15] The SLD can be expressed as the sum of a chemical component[16] (dependent on the concentration of the constituent elements) and a magnetic component (proportional to M).[17] The fits to the R_{++} and R_{--} reflectivities are represented by the solid lines through the spin asymmetry data in Fig. 2, and were generated using reflpol PNR fitting software.[18] The fits match the data well, and correspond to the SLD models shown in Fig. 3. Bracketed by GaAs on either side, the $Ga_{1-x}Mn_xAs$ film shows up clearly in each model, denoted by a region of decreased chemical SLD,[19] and nonzero magnetic SLD. Uncertainty in the models' *net* magnetizations was reconciled by choosing models in which the integrated M is consistent with that obtained from magnetometry measurements.

Annealing changes the depth profiles very little. Both $Ga_{1-x}Mn_xAs$ films feature a pronounced gradient in M that extends over a thickness of approximately 500 ± 100 Å. (Note that—although the fits are not highly sensitive to the exact extent of these gradients—the data unambiguously require that the models' magnetizations near the substrate be greatly depleted.) We therefore conclude that the reduction in net M upon annealing occurs uniformly, and that annealing

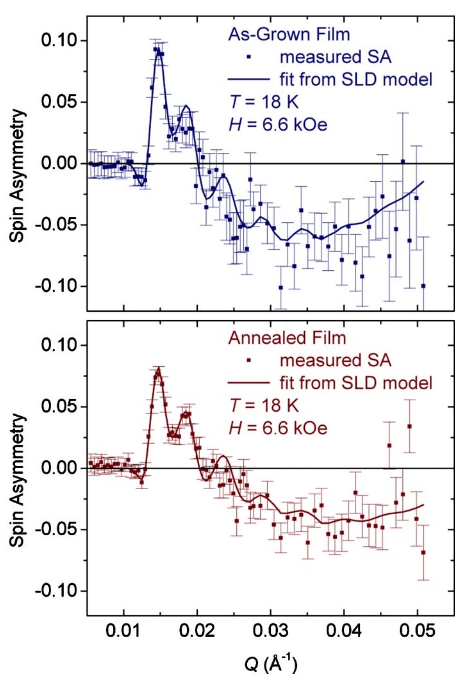

FIG. 2. (Color online) PNR data and fits for the capped samples displayed as spin asymmetry (defined in the text).

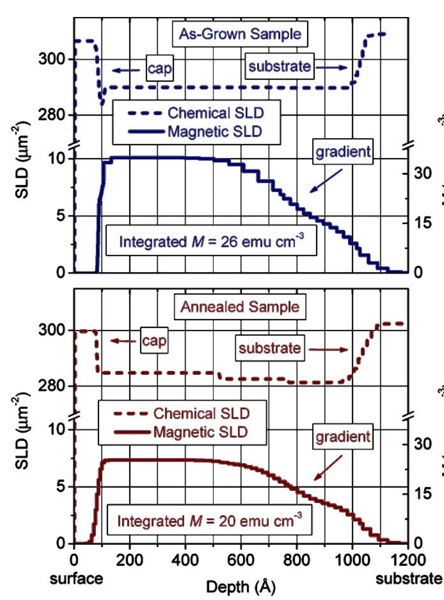

FIG. 3. (Color online) Scattering length density models used to fit the data in Fig. 2.

does not substantially "smooth out" the M gradient. This stands in stark contrast to PNR measurements of the corresponding *uncapped* as-grown/annealed pair[20] (not shown), which do show considerable annealing-dependent differences. The uncapped as-grown film possesses a sloping M profile very similar to the capped as-grown film, but the uncapped annealed film features a large increase in total moment, and a M profile that is significantly smoothed at the substrate interface. However, the uncapped film's M profile did not *completely* flatten during annealing—in contrast to other similar uncapped samples.[11,12] This behavior suggests that this particular annealing (while still sufficient to double the uncapped film's T_C) may have been somewhat less than optimal for both the capped and uncapped samples.

Since M gradients appear to be more prominent for films with lower T_C and net M, it seems likely that they are correlated with increased Mn_I concentration. However, for the models of the capped samples in Fig. 3, the chemical SLD changes little over the region of graded M—implying that the *total* Mn concentration is relatively constant. Therefore, it is likely that the M gradients are indicative of a nonuniform, depth-dependent ratio of Mn_{Ga} to Mn_I, possibly due to small, depth-dependent differences in growth temperature. If this is the case, a M gradient is a "signature" of the Mn_{Ga}/Mn_I ratio. The fact that this signature and the chemical profile change little upon annealing suggests that the cap prevents any large-scale redistribution of Mn_I. This result is consistent with a picture of annealing in which positively charged Mn_I donor ions are prevented from diffusing across a $Ga_{1-x}Mn_xAs/GaAs$ interface in large quantities due to formation of a *p-n* junction,[2,9] and further suggests that the presence of two such interfaces somehow inhibits vertical migration of Mn ions from the outset. However, it is possible that during annealing, a small number of Mn_I *and* Mn_{Ga} do leave their lattice sites and form random Mn clusters or MnAs inclusions. Since the cap appears to prevent *large-scale* surface diffusion of compensating Mn_I, such clustering could result in a small net loss in ferromagnetically active Mn_{Ga}, which would explain the observed drop in T_C and net M.

In summary, we have observed that a GaAs capping layer not only eliminates the beneficial effects of annealing, but it also appears to inhibit annealing's ability to extensively alter the depth-dependence of the magnetization of $Ga_{1-x}Mn_xAs$. These results lend support to a model of annealing for uncapped $Ga_{1-x}Mn_xAs$ in which the added energy pries Mn_I ions from the lattice, allowing them to diffuse toward the free surface. Additionally, we see evidence that a nonuniform magnetization is a common feature of $Ga_{1-x}Mn_xAs$ growth—a factor that may warrant consideration for potential device applications.

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[19] Difference in substrate chemical SLD between the two films is due to differences in reflectometer alignment. These alignment differences do not significantly affect the magnetic SLD, or the distribution of chemical SLD.
[20] A similar uncapped sample that was annealed alongside the capped one—as discussed earlier in the letter.